<u>San Joaquin Valley Study</u>

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The major tasks for the San Joaquin Valley study were to operate two ATOFMS instruments at 2 locations, an urban site in Fresno and a rural site in Angiola. The major list of "deliverables" included the following:

1) Instrument preparation of ATOFMS instruments for field studies beginning in September 2000.

2) December, 2000-January, 2001: Ambient sampling by two ATOFMS instruments plus peripheral equipment.

3) Describe major particle types observed including dust (reacted and unreacted, multiple types), EC, OC, sea salt (reacted and unreacted).

4) Show major associations between major particle types and secondary species including sulfates, nitrates, ammonium, organic species.

5) Prepare final project report briefly detailing findings of ATOFMS instrument, including data for trends in EC, OC, various dust particle types, sea salt, and relative associations with secondary species.

Note the bulk of the deliverables for this project were to actually acquire the data and begin the compilation of the data into a format that could be used for further data analysis as part of a second contract (which is now in place at UC San Diego).

The following represents the final report for a study conducted with two aerosol time-of-flight mass spectrometry (ATOFMS) systems in the San Joaquin Valley. The study was conducted by the Prather Research Group at the University of California, Riverside (now at University of California, San Diego). The ambient aerosol physical and chemical properties were measured as part of the active field campaign associated with the California Regional Particulate Air Quality Study (CRPAQS). The ATOFMS played an important role in the study by recording single particle aerodynamic size and composition data at two sites, Fresno (3425 First Street) and Angiola (trailer – ground level), in the San Joaquin Valley. Several instruments were operated alongside the ATOFMS to provide complementary particulate and atmospheric data. The Fresno site used an optical particle counter (OPC, LASAIR Model 1003) to measure the particle size distribution. The Angiola site had an OPC (LASAIR Model 1003), an aerodynamic particle sizer (APS, TSI, Inc.), and a scanning mobility particle sizer (SMPS, TSI, Inc.) to measure the particle size distribution along with a tapered element oscillating microbalance (TEOM, R&P Model 1400) for particulate mass and a nephelometer (Radiance Research Model M903) for particle radiative properties. The ATOFMS and complementary instrumentation were operated continuously at each site from November 30, 2000 to February 3, 2001 recording approximately 65 days of continuous data less any down-time for instrument maintenance and troubleshooting. The instruments at both sites were operational for each of the four intensive operational phase (IOP) experiments: Dec. 15-18, Dec. 26-28, Jan. 4-7, and Jan. 31-Feb. 3. Both instruments were operated at high laser power to provide an overall analysis of all particle types during each IOP with the exception of the Jan. 4-7 event. This IOP was conducted with the ATOFMS operating at low laser power in an attempt to characterize the organic portion of the PM in more detail.

The ATOFMS dataset acquired for this study at two locations is to date the largest data set for single particle ambient field measurements. The Fresno ATOFMS recorded the size and composition for 1,767,583 single particles over the course of the study. Likewise, the Angiola ATOFMS determined the size and composition of 2,156,904 individual particles. The ATOFMS data for both sites have been compiled into a large database. This database allows rapid searching using rules-based searches. Temporal plots of the number of particles containing any species (or combinations) can be rapidly obtained. The size distribution of the particle types can also be plotted. Figure 1 shows the temporal plot for ATOFMS counts of particles containing

sodium ($Na^+$), potassium ($K^+$), and calcium ($Ca^+$) obtained for Fresno. These particles were obtained by using search criteria to search for all particles with ion peaks at m/z 23, 39, and 40, respectively. The key thing to note in this figure is how the K particles dominate during the fog periods (turquoise), whereas Na (sea salt) and Ca (dust) dominate during other periods. These markers are rapid indicators of the meteorology of the region during this study.

The temporal evolution of particle species within single particles during fog events was examined at Fresno and the Angiola tower site near Corcoran within the San Joaquin Valley, California. The goals of this analysis were to examine the extensive fog and stagnation periods that occur in the valley with emphasis on the formation of particulate matter and the effects of fog on specific harmful chemicals. Using markers in the mass spectra of individual particles, the content of the aerosol is monitored for changes during the fog and stagnation periods. In this analysis, we detected markers indicative of fog processing as described for a previous study conducted in Bakersfield, CA (Whiteaker, 2003). Typical markers for fog processing occur at m/z -81 and -111. Figure 2 shows the temporal evolution of particles containing these markers obtained in Angiola. A strong anti-correlation with ozone levels was observed. This could be due to the fact that ozone levels decrease during fog events. We are still awaiting fog data to corroborate this.

A major goal of this study is to use single particle signatures to determine the major particle types present in this region of California. Apportionment of biomass particles is relatively straightforward. Using single particle data we can further determine the associations between various particle phase species. This provides further clues as to the origin of the dominant species. Figure 4 shows the temporal plot of single particle containing marker ions for aromatic species compared to the trends observed with a photoelectric aerosol sensor (PAS). It is well documented the PAS is sensitive to the concentration of aromatic species. As one can see in this figure, the temporal trends are very similar for two very different instruments. We have just begun making comparisons with data from other instruments in analogy to this in order to gain better insights into aerosol processing in this region. This is one key advantage in participating in a field study of this magnitude. Figure 5 illustrates the comparison of the temporal trends of ATOFMS counts for particles containing PAH, sugar marker ions, against the PAS measurements. Again, it is evident that the PAH species track the biomass burning marker ions, suggesting these species could be originating from the same source. Further analysis is

required to verify this. Finally Figure 6 shows the temporal trends in K-containing particles versus PAH species. Again, there is a strong correlation between wood smoke particles as indicated by K-rich particles and PAH species. It is important to note that K-rich particles can also originate from dust, however single particle spectra with K- from biomass have quite unique chemical combinations compared to those from K-rich dust, making them easy to distinguish between.

Organic species dominated the particles detected in this study. In fact, organic species were observed in particles of all sizes between 0.3 and 3 microns. In studies conducted in other California locations, organics typically dominate the sub-micron fraction. We believe the observed larger sizes are evidence of the effects of fog processing on particle composition. Typical size-resolved distributions were observed after rain events and when weather fronts came through the region. However, as soon as the fog began to build, the larger organic particles were once again observed. Figure 7 shows the typical signature of the organic particles. Significant complexity is observed. This figure shows what we refer to as a digital histogram. The positive and negative ions are both shown. The y-axis represents the percentage of particles containing a specific marker ion. As shown here, the common peaks observed in the organic spectra are 27, 29, 39, 41, 43, 50, 51, 55, 63, 65, 77, and 91. Peaks at 50, 51, 63, 65, 77, and 91 are common fragments of aromatic species. Peaks at higher m/z values are 115, 128, 139, 152, 165, 178, 189, and 202. These higher mass ions are most likely methoxy phenols from wood smoke. These assignments can be made based on previous source testing of wood smoke by Cass and Schauer which reported these species represented a significant fraction of the semivolatile species observed from wood smoke. The combination of the fragmentation patterns in both the positive and negative ion spectra allows for identification. It should be noted that we can only make these assignments based on the fact we know these species were coupled in the same particles. The peaks at 178 and 202 are polycyclic aromatic hydrocarbon species. Note ATOFMS has extremely high sensitivity to aromatic species due to the fact it uses 266 nm radiation for the LDI process. This wavelength induces what is referred to resonance enhanced multiphoton ionization of aromatic species. It is commonly used for detection of trace concentrations of aromatic species in the gas phase. The fact the resonant process occurs enhances its sensitivity for aromatic compounds over non-aromatic (organic) compounds by several orders of magnitude. This is actually an advantage because if we didn't have some level

of selectivity in the LDI process, we would never be able to identify any of the organic peaks. The negative ion digital spectrum is shown below the positive ion spectrum. Ion peaks at m/z -41, -59, and -73 are indicative of sugars found in wood smoke and levoglucosan. Also present in the negative ion spectra are peak due to dihydroxy-benzoquinone (-109) as well as species related to the positive ion aromatic species described above. In Figure 8, the temporal variations of particles whose spectra contain these markers ion are shown. It is obvious from this figure they species peak at night. These species are believed to be semivolatile organic carbon (SVOC) species. Observing these species in real time is an exciting advance as these species have known deleterious health effects. Using traditional filter based sampling techniques, it is difficult to study them due to their volatile nature. There are several possible explanations for the fraction of these particles peaking at night. The most likely reason is these species partition to particles from the gas phase under lower temperature and high relative humidity conditions. These species may also peak at night due to the fact they are emitted in high abundance during the evening hours from wood smoke burning. A third explanation (all may be possible) is there is a much higher surface area of particles available in the evening hours and therefore the species preferentially partition from the gas to the particle phase. One of the goals of this study was to compare particles sampled at a rural site with those sampled at an urban site. An interesting observation is that the strong diurnal trends observed for these species as well as biomass particles are not as apparent in Angiola. The temporal trends of Angiola particles show a slow build up over many days with less day-to-day variability.

Figure 9 shows a summary of the major particle types detected in super-micrometer particles sampled in Fresno during the study. One can see a rapid change in the fraction of organic particles occurred beginning on January 30, 2000. Prior to this event, processed sea salt particles (blue) dominate this size range. However, rapidly these particles are lost during the fog event. The most likely explanation for this is these particles uptake water and become larger and settle out of the atmosphere quickly. The ATOFMS data provide a complete picture of how fast the atmosphere changes due to meteorological events such as fog. This represents an ideal dataset to be compared against models which predict such changes. Such a comparison would provide insight into how well the model is working; if time series for major particle types didn't match the measured data, the models could be improved by adding additional chemistry, for example. As mentioned, the ultimate goal is to break down our data in an analogous manner to

show the relative fractions of particles from different sources; again, it would be quite interesting to compare our data with source oriented model predictions.

Figure 10 shows the association observed for nitrate particles during a fog event in Fresno and Angiola. The most common association is with OC-K particles with ammonium and sulfate. It is likely these particle cores are composed of wood smoke with accumulated ammonium, nitrate, and sulfate. In Angiola, EC particles are the 2nd most dominant class. It was surprising to detect EC particles in Angiola in higher fractions than Fresno. One possibility for this observation is the EC particles have longer atmospheric lifetimes. This has been shown to be the case in Asia for example where long range transport of EC (over OC) has been observed. The key thing to note about particles sampled during fog events is they are highly processed and contain many species, including secondary species. The ability to perform accurate source apportionment in Angiola will be a challenge due to the highly aged nature of the particles.

During this phase of our CRPAQS project, substantial efforts were placed on quantifying the ATOFMS data using MOUDI impactor mass measurements made by Desert Research Institute at both sites during the study. A great deal of time was invested in automating the integration of large ATOFMS datasets with MOUDI mass concentration data collected for multiple sampling periods. This will make the process of scaling ATOFMS data in the future more straightforward. Figure 11 shows the scaling curves adapted by comparing the ATOFMS data with the MOUDI for 6 sampling periods. The curves are similar to those obtained in previous studies. We have obtained similar scaling curves for Angiola. The next step in this project that is being performed in a current contract for this project involves completing the scaling of the ATOFMS data for nitrates, sulfates, ammonium, OC, EC, and metals. In addition, we are using number concentration data collected with SMPS and APS instruments to directly scale the ATOFMS number counts (shown in this report). It is absolutely essential for any future source apportionment work to scale the ATOFMS data before assigning relative contributions from various sources to ambient PM in central California.

We are also developing additional data analysis algorithms that allow us to "cluster" the major particle types based on composition. This will allow for more straightforward source apportionment in the future. Our plans involve using the mass spectral fingerprints of the

clusters as "seeds" to match against source libraries we have created during ATOFMS source tests.

The majority of the goals of this project were to perform the measurements using two ATOFMS instruments over a 2 month period. These measurements resulted in a very exciting set of results with many layers of information that we are currently sorting through. As mentioned, we are continuing with data analysis as part of a data analysis contract for this study. The final report for that project will show data in a scaled format for all major particle types, as well as comparisons with other instruments and meteorological data. Our hopes as part of that project are to begin making an attempt to determine the major sources contributing to PM in this region of California. Ultimately, comparisons will be made between model predictions on the region and ATOFMS data acquired during this study.

Papers directly resulting from this contract:

1.      Whiteaker, J.R. and K.A. Prather, *Detection of pesticide residues on individual particles.* Analytical Chemistry, 2003. **75**(1): p. 49-56.

2.      Whiteaker, J.R. and K.A. Prather, *Hydroxymethanesulfonate as a tracer for fog processing of individual aerosol particles.* Atmospheric Environment, 2003. **37**(8): p. 1033-1043.

3. Qin, X., Whiteaker, J., and K. A. Prather, *The use of single particle SVOC tracers for source apportionment,* in preparation, 2003.